

Appendix CC

Analysis of Canister Data for the Houston-Galveston and Beaumont-Port Arthur Areas

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This analysis of the canister data collected in HGA and BPA produced results that are similar to the results from the Auto-GC analysis performed for the Houston-Galveston SIP Revision in November 2002. The twelve compounds that are generally responsible for high reactivity based on the Auto-GC results are also responsible for high reactivity according to the canister data, in particular propylene and ethylene. The wind direction analysis performed for each of the monitors that collected canister data identified groups of sources that may have been responsible for emitting the compound that contributed most to high reactivity at that monitor, but there were several monitors where the wind directions identified by the analysis did not encompass all of the nearby sources. For eight of the 24 TCEQ monitors that were used in this analysis, the total median reactivity was lowest in the last year of data collection that occurred at each monitor between 1997 and 2001, indicating an overall decrease in concentrations of certain compounds. For the remaining 16 TCEQ monitors, the lowest median reactivity was observed in a year other than the last year, which means that concentrations of some compounds did not decrease overall. The yearly data for all of the South East Texas Regional Planning Commission (SETRPC) monitors showed that concentrations declined to their lowest value in the last year of collected data used for this analysis.

For many of the monitors, either ethylene or propylene accounted for the highest percentage of total reactivity for high reactivity days. For monitors located in the HGA area, wind direction analysis has indicated that the emissions from the Ship Channel area have contributed to high ethylene and propylene concentrations.

Introduction

Previous analysis of volatile organic compounds (VOCs) has primarily depended on concentration data collected at Auto-GC sites. The purpose of this project is to extend that analysis to the 24-hour canister samples collected at several monitors in the Houston-Galveston (HGA) and Beaumont-Port Arthur (BPA) areas. This summary of that analysis focuses on the data collected at both Texas Commission on Environmental Quality (TCEQ) and South East Texas Regional Planning Commission (SETRPC) canister sites in the Beaumont area and TCEQ sites in the Houston area. There are two key questions regarding this data that the analysis will attempt to answer. These questions are as follows:

- Which compounds are most important in the formation of ozone in the HGA and BPA areas?
- What is the relationship between concentration and wind direction for this data?

The first of these two questions is important in that previous analysis of VOC emissions in the HGA area has identified several compounds and groups of compounds that are generally thought to be responsible for high ozone, but this analysis has not been performed using the canister data.

It is important to know if the canister data support the previous findings as to which compounds are responsible for high ozone. There are no monitors to collect Auto-GC data in the BPA area, so it is especially important to analyze the canister data for this area to make sure that the compounds that are important in causing high reactivity in BPA are similar to the ones causing high reactivity in HGA. Also, this data may lead to identification of other compounds that play an important role in the formation of ozone. The second question is important because wind direction analysis of this 24-hour data can point to the sources that are responsible for high concentrations of a given VOC.

Analysis Methods

Data availability

VOC data is collected at seven TCEQ monitors and six SETRPC monitors in the Beaumont-Port Arthur (BPA) area and at seventeen TCEQ monitors in the Houston-Galveston (HGA) area. Three of the BPA SETRPC monitors are co-located with TCEQ monitors. All of the samples collected at these sites are 24-hour samples collected in canisters; the TCEQ monitors collect new samples every six days and the SETRPC monitors collect new data every twelve days. For this analysis, only the data collected between 1997 and 2001 was used. **Table I-1** gives a summary of the data available for each of the BPA monitors, and **Figure I-1 (App. I)** shows the locations of the BPA sites. **Table I-2** and **Figure I-2 (App. I)** give similar information for the HGA monitors.

Table I-1.
Site information for the BPA monitors

Monitor Type	Sitename	AIRS Code	Dates of Collection	Number of Samples
SETRPC	Airport		Jan. 4, 1997 - Dec. 21, 2001	110
SETRPC	Beaumont		Jan. 4, 1997 - Dec. 21, 2001	138
SETRPC	Cove School		Jan. 4, 1997 - Dec. 21, 2001	142
SETRPC	Mauriceville		Jan. 11, 1997 - Dec. 21, 2001	116
SETRPC	Port Neches		Jan. 4, 1997 - Dec. 21, 2001	143
SETRPC	West Orange		Jan. 4, 1997 - Dec. 21, 2001	141
TCEQ	Beaumont C2	482450009	Jan. 4, 1997 - Dec. 21, 2001	274
TCEQ	Port Arthur West C28	482450011	Jan. 4, 1997 - Dec. 27, 2001	279
TCEQ	Groves C119	482450014	Jan. 16, 1997 - Dec. 27, 2001	219
TCEQ	Port Neches C136	482450017	Jan. 4 1997 - Dec. 27, 2001	272
TCEQ	City Service Center/PA C131	482450019	May 22, 1997 - Dec. 27, 2001	219
TCEQ	Carroll St. Park C54	482450020	Feb. 10, 1998 - Dec. 21, 2001	192
TCEQ	West Orange C9	483611001	Jan. 4, 1997 - Dec. 27, 2001	270

Table I-2
Site information for the HGA monitors

Monitor Type	Site Name	AIRS Number	Dates of Collection	Number of Samples
TCEQ	Clute C11	480391003	Jan. 4, 1997 - Dec. 27, 2001	248
TCEQ	Texas City Ball Park C147	481670005	Nov. 18, 1997 - Nov. 27, 2001	175
TCEQ	Galveston Airport C34	481670014	Jan. 4, 1997 - Dec. 27, 2001	273
TCEQ	Texas City C100	481670053	Jan. 4, 1997 - Dec. 21, 2001	209
TCEQ	Aldine C8	482010024	Jan. 4, 1997 - Dec. 27, 2001	287
TCEQ	Channelview C15	482010026	Jan. 10, 1997 - Dec. 21, 2001	257
TCEQ	Northwest Harris Co. C26	482010029	May 5, 1998 - Dec. 21, 2001	203
TCEQ	Bayland Park C53	482010055	Apr. 17, 1998 - Dec. 21, 2001	192
TCEQ	Galena Park C167	482010057	Nov. 6, 1997 - Dec. 27, 2001	205
TCEQ	Baytown C148	482010058	Apr. 17, 1998 - Dec. 27, 2001	185
TCEQ	Shore Acres C145	482010061	July 22, 1998 - Dec. 27, 2001	194
TCEQ	Allendale C120	482010064	Jan. 4, 1997 - Mar. 25, 1999	106
TCEQ	Milby Park C169	482010069	Apr. 12, 1999 - Dec. 27, 2001	119
TCEQ	HRM-3 Haden Road C603	482010803	Jan. 4, 1997 - Dec. 27, 2001	260
TCEQ	Clinton	482011035	Jan. 4, 1997 - Dec. 27, 2001	249
TCEQ	Deer Park	482011039	Jan. 4, 1997 - Dec. 27, 2001	263
TCEQ	San Jacinto Monument C166	482011041	Apr. 24, 2000 - Oct. 4, 2001	81

Compound groups

The compounds collected at each monitor were grouped according to structural similarity in order to reduce the number of categories on the graphs used to analyze the data. Twelve of the compounds measured at the monitors had already been identified as contributors to high ozone by previous VOC analysis. These twelve compounds are ethylene, propylene, 1,3-butadiene, isoprene, styrene, toluene, 1-pentene, isopentane, n-butane, 1-butene, m & p-xylene, and 1,2,4-trimethylbenzene; each of these compounds was included with the proper group or was put into its own group. Since different compound concentrations were measured at the TCEQ and SETRPC monitors, the grouping of compounds was slightly different for each set of monitors. The names of the groups along with the compounds included in each group for each set of monitors are given in **Table I-3**.

Table I-3. Compound Groups

Group Name	TCEQ Compounds	SETRPC Compounds
Ethylene	Ethylene	Ethylene
Propylene	Propylene	Propylene
Butadiene	1,3-Butadiene	1,3-Butadiene
Isoprene	Isoprene	Isoprene
Styrene	Styrene	Styrene
Toluene	Toluene	Toluene
MTBE	MTBE	MTBE
Butenes	1-Butene; c-2-Butene; t-2-Butene	1-Butene
Pentenenes	1-Pentene; 2-Methyl-2-Butene; 3-Methyl-1-Butene; c-2-Pentene; t-2-Pentene	1-Pentene
Large Alkenes	1-Hexene-2-Methyl-1-Pentene; 1-Heptene; 2-Methyl-1-Pentene; 4-Methyl-1-Pentene; c-2-Hexene; t-2-Hexene	1-Hexene-2-Methyl-1-Pentene; 1-Octene
C2C3	Ethane; Propane; Acetylene	Ethane; Propane
Butanes	n-Butane; Isobutane	n-Butane
Pentanes	Isopentane; n-Pentane	Isopentane; n-Pentane
Alkanes	2-2-4-Trimethylpentane; 3-Methylpentane; n-Octane; n-Decane; n-Hexane; 2,4-Dimethylpentane; 2-Methylheptane; 2-Methylhexane; 3-Methylheptane; 2-Methylpentane_Isohexane; n-Heptane; 3-Methylhexane; n-Nonane; n-Undecane; 2,3-Dimethylpentane; 2,3-Dimethylbutane; 2,3,4-Trimethylpentane; 2,2-Dimethylbutane_Neohexane	2-2-4-Trimethylpentane; 3-Methylpentane; n-Octane; n-Decane; n-Hexane; Isohexane
Xylenes	o-Xylene; p-Xylene + m_Xylene	o-Xylene; p-Xylene + m_Xylene
Aromatics	Benzene; Ethylbenzene; Isopropylbenzene; m-Diethylbenzene; n-Propylbenzene	Benzene; Cumene; Naphthalene; t-Butylbenzene
Trimethylbenzenes	1,2,3-Trimethylbenzene; 1,2,4-Trimethylbenzene; 1,3,5- Trimethylbenzene	1,2,4-Trimethylbenzene
Ethyltoluenes	m-Ethyltoluene; o-Ethyltoluene; p-Ethyltoluene	
Cyclos	Cyclohexane; Methylcyclohexane; Methylcyclopentane; Cyclopentane; Cylcopentene	Cyclohexane; Methylcyclohexane

Group Name	TCEQ Compounds	SETRPC Compounds
Halogenates	1,2-Dichloroethane; Carbon Tetrachloride; Chlorobenzene; Chloroform; Chloroprene; Trichlorofluoromethane; Vinyl Chloride; Methylene Chloride; Trichloroethylene; Trichlorofluoromethane; 2-Chloropentane; Bromomethane; cis-1,3-Dichloropropylene; 1,1-Dichloroethane; 1,1-Dichloroethylene; 1,2-Dibromoethane; 1,2-Dichloropropane; trans-1,3-Dichloropropylene; 1,1,2,2-Tetrachloroethane; 1,1,2-Trichloroethane; Tetrachloroethylene_Perchloroethylene	1,1,1-Trichloroethane; 1,2-Dichloroethane; Carbon Tetrachloride; Chlorobenzene; Chloroform; Trichlorofluoromethane; Methylene Chloride; Trichloroethylene; Vinyl Chloride; 1,1,1-Trichloroethane; Trichlorofluoromethane
Monoterpenes	a-Pinene; b-Pinene	a-Pinene; b-Pinene

MIR Reactivity

Each of the compounds measured in the canisters reacts with other compounds in the air to form ozone at different rates and in different amounts. For this reason, reactivity values, rather than pure concentration data, were used to weight the contribution to total ozone formation in favor of compounds that have the potential to form large quantities of ozone quickly. There are two types of reactivity scales that can be used to assign ozone formation potential to a given VOC compound; these scales are OH reactivity and maximum incremental reactivity (MIR). The OH reactivity scale is used to give an idea of how fast a compound will begin participating in reactions to form ozone; the MIR scale is used to give an idea of how much ozone a compound can form. For this analysis, only the MIR scale was used (Carter, 2002). The MIR value for each of the compounds measured in the canisters was calculated by multiplying the compound's concentration in ppbV by an MIR conversion factor, which consists of the MIR constant multiplied by the ratio of the molecular weight of the VOC to the molecular weight of ozone. The total reactivity for each group of compounds was found by summing the reactivities of all of the compounds falling within that group.

Description of analysis

One group of samples that were of particular interest were the samples with high reactivity. The method used to identify high reactivity days involved calculating the total MIR for each sample by summing the group reactivities and finding the 90th percentile of the total reactivity for all of the samples at a given monitor. All of the samples with a total reactivity higher than the 90th percentile were separated from the rest of the data and the median reactivity for each compound group was calculated. These median values were used to create pie charts that compared the contribution to high reactivity of all of the compound groups for a given monitor.

In order to determine whether or not the contribution of certain compound groups to total reactivity had increased or diminished at a given monitor over the time period used in this analysis, stacked bar charts were created using the median reactivity for each compound group over an entire year at that monitor. All of the samples collected within a year, not just the samples with high reactivity, were used to find the median values. Each bar represents one year in the time span and the reactivity groups are represented by the colored bands.

The first step in the wind direction analysis was to merge wind direction and speed data with the canister concentration data, which resulted in as many as 24 different hourly wind directions for each VOC sample. The wind direction values were rounded to the nearest ten to create ten degree wind bins. The data were sorted by site and wind bin, and the arithmetic and geometric mean concentrations were calculated by monitor and wind bin for each of the twelve compound groups that are known to contribute to high ozone. These mean values were plotted versus wind bin and fitted with an interpolated curve to show the distribution of the high and low concentrations of each compound. One plot was created for each compound at each monitor. This wind direction analysis method was developed by Dave Sullivan. These wind direction plots were used along with maps of industrial VOC sources to identify which of the industrial sources could be contributing to high VOC levels at each monitor. Wind analysis could not be performed for the six SETRPC sites in BPA and for two of the TCEQ sites in HGA because there is no wind direction and speed data available for these sites.

Results

The first part of the analysis involved using high reactivity samples to determine the compounds that make the largest contributions to total reactivity in those high reactivity samples. Pie charts were created for all of the monitors, with each piece representing a different compound group. The top four contributors to reactivity for each of the TCEQ sites are summarized in **Tables I-4 and I-5**; in some cases where several compounds tie for fourth place, only the top three compounds are given.

Table I-4. Top four compounds contributing to high reactivity at BPA monitors

Site Name	Compound	%	Compound	%	Compound	%	Compound	%
482450009	Ethylene	19	Propylene	13	Pentanes	10		
482450011	Ethylene	23	Butanes	17	Pentanes	12	Butenes	11
482450014	Butanes	31	Pentanes	17	Butenes	13	Pentenes	10
482450017	Butadiene	57	Butenes	13	Ethylene	7	Propylene	6
482450019	Propylene	33	Pentanes	15	Ethylene	14	Butanes	9
482450020	Propylene	16	Butenes	15	Ethylene	12	Pentanes	11
483611001	Ethylene	22	Pentenes	12	Pentanes	11	Butanes	10
Airport	Ethylene	31	Pentanes	16	Propylene	9	Butanes	8
Beaumont	Xylenes	19	Pentanes	17	Ethylene	16	Toluene	8
Cove School	Ethylene	52	Propylene	8	Alkanes	7	Pentanes	5
Mauriceville	Xylenes	23	Ethylene	16	Isoprene	11	Pentanes	7
Port Neches	Butadiene	58	Ethylene	9	Propylene	6		
West Orange	Ethylene	62	Propylene	7	Butadiene	4	Alkanes	4

Table I-5

Top four compounds contributing to high reactivity at HGA monitors

Site Name	Compound	%	Compound	%	Compound	%	Compound	%
480391003	Ethylene	87	Propylene	6	Cyclos	2		
481670005	Butenes	20	Propylene	15	Pentanes	12	Pentenenes	9
481670014	Propylene	22	Ethylene	19	Butanes	11	Butenes	10
481670053	Propylene	25	Butenes	21	Ethylene	10	Pentanes	10
482010024	Ethylene	13	Propylene	13	Butenes	9	Pentenenes	9
482010026	Propylene	36	Ethylene	18	Butanes	10	Butenes	7
482010029	Propylene	19	Ethylene	16	C2C3	11	Butanes	11
482010055	Propylene	16	Ethylene	16	Butenes	10	Butanes	8
482010057	Propylene	17	Ethylene	14	Butenes	13	Butanes	10
482010058	Propylene	60	Ethylene	14	Butenes	8	Pentenenes	4
482010061	Propylene	43	Ethylene	16	Butanes	8		
482010064	Butenes	35	Propylene	17	Ethylene	11	Butadiene	9
482010069	Butenes	29	Pentenenes	12	Propylene	11	Butanes	10
482010803	Propylene	23	Ethylene	17	Butenes	12	Butanes	10
482011035	Butenes	15	Butanes	15	Propylene	12	Ethylene	10
482011039	Propylene	42	Ethylene	18	Butenes	6	Butanes	6
482011041	Propylene	81	Ethylene	5	Butenes	2	Pentanes	2

For over half of the samples in both HGA and BPA, either propylene or ethylene is the top contributor to reactivity, and 23 of the 30 monitors contain both propylene and ethylene in the top four compounds. Butanes, butenes, pentanes, and pentenes are also significant contributors to high reactivity at several of the sites.

In the following sections of this report, each of the monitors used in this analysis will be discussed. The results from the wind direction analysis and the comparison of yearly reactivity will be included in these sections for the TCEQ monitors, and figure numbers for the graphs and maps created for each monitor will be given. The seven BPA TCEQ monitors will be discussed first, followed by the six BPA SETRPC monitors and the 17 HGA monitors.

482450009 Beaumont (Figs. I-3 through I-6, App. I)

Ethylene is the biggest contributor to high reactivity at this site. The wind direction analysis indicates that there are high ethylene concentrations in wind coming from the northeast and from the southeast; these wind directions are indicated on the map by the sets of blue lines. The map of ethylene sources shows that there is a large group of sources to the north and northeast of the monitor, some of which are included in the wind direction span that points to the northeast. There is also a smaller group of sources that fall within the wind span to the southeast that

corresponds to the second peak in ethylene concentration. The yearly data given by the bar chart indicate that reductions in ethylene, propylene, toluene, and cyclo compounds led to much lower overall reactivity in 1998 than was seen in 1997, but an increase in ethylene concentrations led to higher reactivity in 1999. The data for 2000 and 2001 were deleted as a result of very high xylene concentrations that were considered inaccurate.

482450011 Port Arthur West (Figs. I-7 through I-10, App. I)

Similar to the Beaumont monitor, ethylene is biggest contributor to high reactivity at the Port Arthur West monitor, although there are several compounds that are responsible for more than ten percent of the total reactivity. The wind direction plot for this monitor indicates that there are high ethylene concentrations in wind coming from the south (around 190°), which is the wind direction marked by the light blue lines on the ethylene source map. The largest group of ethylene sources in the area of this monitor falls within the wind direction span indicated by the plot, which indicates that these sources are most responsible for ethylene concentrations seen at this monitor. The yearly data shows that steady reductions in the concentration of butanes, butenes, alkanes, toluene, and ethylene have driven the overall reactivity observed at the monitor lower over the five years between 1997 and 2001.

482450014 Groves (Figs. I-11 through I-14, App. I)

At this monitor, butanes are responsible for the largest portion of total reactivity for the high reactivity samples. This monitor is unlike most of the other monitors in that neither ethylene nor propylene contribute enough to total reactivity to be listed in the top four compounds. Wind direction data show that elevated butane concentrations appear in wind from the east to southeast, and the range of wind directions with elevated concentrations are shown on the source map by the pink lines. Within this range of wind directions, there are several small butane sources, but all of the large sources in the area of this monitor are located to the north, where the butane concentrations shown by the wind direction plot are much lower. The yearly data shows that the overall reactivity measured at the monitor was higher in 2001 than in any of the other years, and this increase in reactivity is primarily the result of high concentrations of butanes.

482450017 Port Neches (Figs. I-15 through I-18, App. I)

The compound 1,3-butadiene accounts for over half of the reactivity observed at this monitor on high reactivity days, and the wind direction analysis indicates that most of the elevated concentrations of 1,3-butadiene occur in winds from the northeast to southeast. The butadiene source map shows that there are several sources that are located within this range of wind directions, and that there are many other butadiene sources located around the monitor that do not fall within the specified wind direction range. The lowest overall reactivity observed in the yearly data occurred in 2001 as a result of significant reductions in butadiene and butene concentrations throughout the previous four years.

482450019 City Service Center (Figs. I-19 through I-22, App. I)

Propylene accounts for approximately one third of the total reactivity measured at the City Service Center monitor for high reactivity days. The winds that have the highest propylene concentrations come from the northeast to southeast. The wind direction range indicated on the propylene source map for this monitor does encompass many of the closest large propylene

sources, but there are also several groups of sources nearby that do not appear to contribute to high propylene concentrations based on the wind direction plot. Decreases in the concentration of ethylene, butenes, and alkanes led to an overall decrease in total reactivity between 1997 and 2001, although there was little change in total reactivity between 2000 and 2001.

482450020 Carroll St. Park (Figs. I-23 through I-26, App. I)

There are several compounds measured at the Carroll St. Park monitor that account for ten percent or greater of the total high reactivity, but propylene accounts for the largest percentage of that total. Wind direction data show that elevated propylene concentrations are present in winds coming from the east and southeast. There are many propylene sources located close to the monitor throughout the north, east, and southeast. The range of wind directions provided by the wind direction plot do encompass some of these sources, but there are also many that fall outside of this direction range and do not appear to be causing elevated propylene concentrations at the monitor based on the wind direction plot. The yearly median data show that decreases in butenes, butanes, and xylenes led to decreases in reactivity from 1998 to 2000, but an increase in isoprene and alkanes caused reactivity to increase between 2000 and 2001.

483611001 West Orange (Figs. I-27 through I-30, App. I)

The most sizeable contributor to high reactivity at the West Orange monitor is ethylene. The wind direction analysis for this monitor shows a sharp increase in mean ethylene concentrations for wind coming out of the southeast and south. The span of wind directions with elevated ethylene concentrations is shown on the source map by the blue lines; there is a big group of sources located within this span of directions that could account for the higher concentrations. After increasing dramatically in 1998, the yearly data show that ethylene concentrations, and overall reactivity, have dropped between 1998 and 2001. The drop in ethylene between 2000 and 2001 is partially offset by an increase in butanes and pentanes, so that the total reactivity observed at this monitor in 2001 is approximately equal to the total observed in 2001; both of these totals are lower than those measured in the previous three years.

Airport SETRPC (Figs. I-31 and I-32, App. I)

Ethylene is the biggest contributor to high reactivity at the Airport SETRPC monitor, accounting for over 30 percent of the total reactivity. The yearly data indicate that increases in ethylene, pentanes, and alkanes led to a slight increase in overall reactivity between 1997 and 1998. The total reactivity value did not change significantly in 1999, but drastic reductions in ethylene and propylene concentrations led to a much lower total in 2001. The data for 2000 was not available.

Beaumont SETRPC (Figs. I-33 and I-34, App. I)

Xylenes, pentanes, and ethylene are the biggest contributors to high reactivity at the Beaumont SETRPC monitor, with the xylenes compound group contributing almost 20 percent of the total reactivity. This xylenes concentration is higher than at many of the other monitors, although xylenes concentrations were also fairly high at the Beaumont TCEQ monitor. There was little change in the total median reactivity between 1997 and 1999. Reactivity increased slightly in 2000 as a result of increases in the concentrations of xylenes, pentanes, and alkanes. Reactivity dropped to its lowest value in 2001 when concentrations of xylenes also dropped to their lowest value.

Cove School SETRPC (Figs. I-35 and I-36, App. I)

Over 50 percent of the total median reactivity for high reactivity days observed at the Cove School SETRPC monitor is contributed by ethylene. Significant reductions in the concentration of this compound, along with reductions in butadiene and propylene led to the lowest total median reactivity in 2001. Concentrations of ethylene and propylene had fluctuated throughout the other four years of data, and an increase in the concentrations of butadiene, pentanes, and propylene led to the highest total reactivity in 2000, before reactivity dropped the next year.

Mauriceville SETRPC (Figs. I-37 and I-38, App. I)

Xylenes, ethylene, and isoprene are the biggest contributors to high reactivity at the Mauriceville SETRPC monitor, with the xylenes compound group contributing over 20 percent of the total reactivity. This xylenes concentration is higher than at many of the other monitors, although xylenes concentrations were also fairly high at the Beaumont SETRPC monitor. There was little change in the total median reactivity between 1998 and 2001, although a slight reduction in ethylene and butadiene resulted in a slightly lower total reactivity.

Port Neches SETRPC (Figs. I-39 and I-40, App. I)

As with the Port Neches TCEQ monitor, the compound 1,3-butadiene accounts for over half of the reactivity observed at the Port Neches SETRPC monitor on high reactivity days. The yearly data show a steady reduction in ethylene, butadiene, and butenes concentrations, resulting the lowest total median reactivity observed in 2001.

West Orange SETRPC (Figs. I-41 and I-42, App. I)

For high reactivity days observed at the West Orange SETRPC monitor, ethylene contributes over 60 percent of the total reactivity; ethylene is also the biggest contributor to total reactivity on high reactivity days at the West Orange TCEQ monitor. The yearly median concentration chart shows that between 1997 and 2001, the total median reactivity has steadily decreased as a result of large decreases in ethylene and smaller decreases in propylene.

480391003 Clute (Figs. I-43 through I-46, App. I)

Ethylene is by far the biggest contributor to high reactivity at the Clute monitor, and accounts for nearly 90 percent of the total for high reactivity days. All of the largest ethylene sources near the Clute monitor fall within the range of directions to the southwest that have winds with high ethylene concentrations according to the wind direction plot. There are several small sources outside of this degree range that may have caused the smaller bumps in the wind direction plot for winds from the east and northeast. The yearly data show that over the five years used in this analysis, ethylene and propylene are the biggest overall contributors to reactivity. Propylene concentrations have fluctuated and have not achieved significant reductions, but ethylene has been reduced overall to result in the lowest reactivity in 2001 in spite of the increase in concentration of many of the other significant compounds.

481670005 Texas City Ball Park (Figs. I-47 through I-50, App. I)

The primary contributor to high reactivity at this site is the butenes compound group, and propylene is also a significant contributor. The wind direction plot shows that butene concentrations are elevated in winds coming from a large range of wind directions that extends from approximately 50° to 225°. The sources shown on the map for this monitor are 1,3-

butadiene sources, but butenes are often emitted with butadiene, and errors occurred in trying to find the butene sources in this area. The span of wind directions indicated in the plot encompasses almost all of the sources in the area, with the exception of a few that are in the southwest and northwest. The yearly median data for the five years of collection used in this analysis shows that reactivity reached its peak in 1998, but decreases in the concentration of ethylene, butenes, pentanes, and xylenes led to the second lowest reactivity in 2001. According to the bar chart, the lowest reactivity actually occurred in 1997, but data for this year was only collected beginning on Nov. 18, so the low reactivity may be a result of the fact that all of the data for 1997 is winter data, so concentrations and reactivity may be lower.

481670014 Galveston Airport (Figs. I-51 through I-54, App. I)

Propylene and ethylene make up a significant portion of the total reactivity observed at this monitor for high reactivity days, although propylene does account for a slightly larger portion than ethylene. The wind direction data show that the highest propylene concentrations occur in winds coming from the northwest, and the source map shows that all of the biggest propylene sources in the area of this monitor are located to the northwest. The yearly data show that the median propylene concentration measured in 2001 is lower than the median concentrations measured in 1997 and 1999 and is approximately equal to the median concentration measured in 2000, but an increase in the median ethylene concentration, along with the increased concentrations of C2C3 compounds, butanes, and pentanes, led to an increase in total reactivity between 2000 and 2001.

481670053 Texas City (Figs. I-55 through I-58, App. I)

Propylene and butenes are the two biggest contributors to high reactivity at the Texas City monitor, with propylene contributing a quarter of the total reactivity. According to the wind direction analysis, high propylene concentrations measured at this monitor come primarily from wind blowing out of the southeast to southwest. The source map for this monitor shows that many of the small propylene sources in this area and all of the large sources are included within the span or wind directions indicated by the wind direction analysis. After dropping steadily between 1997 and 1999, the total reactivity for the Texas City monitor increased in 2000 and then dropped again in 2001, so that the total reactivity for 2001 was approximately equal to the total reactivity in 1999. The median propylene concentration was the lowest in 2001.

482010024 Houston Aldine (Figs. I-59 through I-62, App. I)

Both ethylene and propylene contribute equally to high reactivity at the Aldine monitor. The wind direction plot is only given for propylene, but the ethylene plot is very similar, so the wind direction range marked on the source map that indicates where the highest concentrations are coming from is valid for both compounds. There are not many ethylene or propylene sources near the Aldine monitor; most of the sources are located to the southeast along the Houston Ship Channel. The wind direction range indicated by the propylene wind direction plot points to the southeast, and many of the propylene and ethylene sources along the Ship Channel are encompassed within this wind direction range, although some of the largest ethylene sources are outside of it. The yearly data for 2000 and 2001 was deleted as a result of erroneously high xylene concentrations, but the median concentration data for 1997 through 1999 show that ethylene and propylene decreased from 1997 to 1998, but then increased in 1999. The median propylene concentration observed in 1999 is higher than in the previous years, but the total

reactivity is still less than the total reactivity for 1997 because of reductions in several other compounds, such as pentenes.

482010026 Channelview (Figs. I-63 through I-66, App. I)

For high reactivity days observed at the Channelview monitor, propylene contributes over one third of the total reactivity and twice the percentage of the next highest compound, ethylene. Wind direction analysis indicates that the highest ethylene concentrations come with winds out of the southeast. The range of wind directions indicated on the source map cover a cluster of small sources on the eastern side of Galveston Bay, but does not include any of the propylene sources along the Ship Channel or a group of fairly large sources located very close to the monitor to the north. The yearly median concentration chart shows that between 1997 and 2001, the propylene concentration has increased overall, but the butadiene, butenes, and xylenes concentrations have all decreased. The total reactivity observed in 2001 is slightly greater than the totals for 1999 and 2000, but is still lower than the total observed in 1997.

482010029 Northwest Harris Co. (Figs. I-67 through I-70, App. I)

The primary contributor to high reactivity at the Northwest Harris County monitor is propylene. The wind direction plot shows that propylene concentrations are elevated in winds coming from a range of wind directions that extends from approximately 70° to 140°. This monitor is located to the northwest of the Houston Ship Channel, and there are few significant propylene sources located nearby. Since the range of wind directions does point to the southeast, it is possible that the sources in the Ship Channel are responsible for the elevated concentrations coming from this direction although the monitor is located fairly far away from this area. The yearly median data for the four years of collection used in this analysis shows that reactivity reached its lowest value in 2000, but increases in the concentration of C2C3 compounds, butenes, butanes, and alkanes led to the second highest total reactivity in 2001.

482010055 Bayland Park (Figs. I-71 through I-74, App. I)

Propylene and ethylene each contribute 16 percent of the total reactivity observed at the Bayland Park monitor for high reactivity days, although propylene does account for a slightly higher median reactivity percentage than ethylene. The wind direction data show that the highest propylene concentrations occur in winds coming from the northeast to southeast, and the source map shows that the Houston Ship Channel, which contains all of the biggest propylene sources in the area of this monitor, is located to the east of the monitor. The yearly data show that total reactivity was the lowest in 2000 and that increases in the concentrations of propylene, C2C3 compounds, isoprene and toluene, along with other compounds, led to an increase in total reactivity between 2000 and 2001.

482010057 Galena Park (Figs. I-75 through I-78, App. I)

There are several compounds measured at the Galena Park monitor that account for ten percent or greater of the total high reactivity, but of these compounds, propylene accounts for the largest percentage. Wind direction data show that elevated propylene concentrations are present in winds coming from the east and southeast. There are many propylene sources located close to the monitor throughout the south, east, and southeast. The range of wind directions provided by the wind direction plot do encompass some of these sources, but there are also many that fall outside of this direction range to the south along the Ship Channel and do not appear to be

causing elevated propylene concentrations at the monitor based on the wind direction plot. The yearly median data show that decreases in butenes, pentenes, butanes, and alkanes led to decreases in reactivity from 1997 to 2000, but increases in all of these compounds caused reactivity to increase between 2000 and 2001.

482010058 Baytown (Figs. I-79 through I-82, App. I)

Propylene is by far the biggest contributor to high reactivity at the Baytown monitor, and accounts for 60 percent of the total for high reactivity days. The wind direction analysis for the Baytown monitor shows that there are two wind direction ranges with high propylene concentrations, one to the southeast and one to the southwest. Most of the propylene sources near the Baytown monitor fall within one of these wind direction ranges with the exception of a few small groups to the south and west, which may account for the elevated concentrations to the west and south shown on the wind direction plot. The yearly data show that ethylene and propylene have been the biggest overall contributors to reactivity. The concentrations of both of these compounds have fluctuated over the four years between 1998 and 2001, but overall, the ethylene and propylene concentrations are less in 2001 than they were in 1998 and the total reactivity measured in 2001 is lower than the total for any other year.

482010061 Shore Acres (Figs. I-83 through I-86, App. I)

Propylene and ethylene make up a significant portion of the total reactivity observed at this monitor for high reactivity days, although propylene does account for more than twice the contribution of ethylene. The Shore Acres monitor is located to the southeast of the Ship Channel, and the wind direction data show that the highest propylene concentrations occur in winds coming from the northwest. Many of the propylene sources in the area are in the Ship Channel area and are encompassed by the wind direction range obtained from the wind direction plot. The yearly data show that after an increase in reactivity between 1998 and 1999, overall decreases in propylene, butenes, alkanes, xylenes, and toluene concentrations led to progressively lower reactivity totals, with the lowest total occurring in 2001.

482010064 Allendale (Figs. I-87 and I-88, App. I)

Butenes account for 35 percent of the total reactivity measured at the Allendale monitor, which is more than twice the percentage of the next highest compound, propylene. There was no wind direction data collected at this monitor over the time period used for this analysis, so no wind direction analysis was performed for this monitor. The yearly median data show that decreases in the concentrations of pentenes, C2C3 compounds, alkanes, and several other compound groups led to a total reactivity in 2001 that was lower than the total for either of the other two years of data.

482010069 Milby Park (Figs. I-89 through I-92, App. I)

The primary contributor to high reactivity at this site is the butenes compound group. The wind direction plot shows that butene concentrations are elevated in winds coming from a range of wind directions that extends from approximately 100° to 180°. As with the Texas City Ball Park monitor, the sources shown on the map for this monitor are 1,3-butadiene sources, but butenes are often emitted with butadiene, and errors occurred in trying to find the butene sources in this area. The span of wind directions indicated in the plot encompasses a group of sources located very close to the monitor to the southeast, but excludes many of the sources located to the north

and northeast along the Ship Channel. The yearly median data for the three years of collection used in this analysis show that reactivity reached its lowest value in 2000, but increases in the concentration of ethylene, butenes, and propylene, along with increases in other compounds, led to the second highest reactivity in 2001.

482010803 HRM-3 Haden Road (Figs. I-93 and I-94, App. I)

Propylene and ethylene make up a significant portion of the total reactivity observed at the HRM-3 monitor for high reactivity days, although propylene does account for a higher percentage than ethylene. There is no wind direction data available for this monitor, so the wind direction analysis was not performed. The yearly data show that the median propylene concentration measured in 1998 was greater than the median concentrations measured in 1998, but after 1998, propylene and ethylene concentrations, along with total median reactivity, steadily decreased until 2000. A sizeable increase in the median propylene concentration in 2001 caused the total median reactivity for 2001 to increase.

482011035 Clinton (Figs. I-95 through I-98, App. I)

The primary contributor to high reactivity at the Clinton monitor is the butenes compound group. The wind direction plot shows that butene concentrations are elevated in winds coming from a range of wind directions that extends from approximately 160° to 210°. As with several of the other monitors, the butenes group is the biggest contributor to high reactivity, but the sources on the map are butadiene sources because there were errors in trying to find the butenes sources. This should not present a problem since butenes and butadiene are often emitted together. This monitor is located to the north of the Houston Ship Channel, and there are few significant propylene sources located nearby other than those located along the channel. The range of wind directions does point to the south and does encompass two large groups of butene emitters, but there are several other groups located to the east that do not appear to be contributing to elevated concentrations in the wind direction plot. The yearly median data for the four years of collection used in this analysis shows that reactivity reached its lowest value in 2000, but increases in the concentration of butenes, butanes, pentenes, and pentanes led to an increase in total reactivity in 2001.

482011039 Deer Park 2 (Figs. I-99 through I-102, App. I)

Propylene and ethylene are the two biggest contributors to high reactivity at the Texas City monitor, with propylene contributing over 40 percent of the total reactivity. According to the wind direction analysis, high propylene concentrations measured at this monitor come primarily from wind blowing out of the northeast between 10° and 60°. The source map for this monitor shows that many of the small propylene sources in this area and all of the large sources are included within the span or wind directions indicated by the wind direction analysis. After dropping between 1997 and 1998, the total reactivity for the Texas City monitor increased in 1999, primarily as a result of a significant increase in propylene and ethylene concentrations, and then dropped again in 2000, as a result of decreases in the concentrations of almost every compound. The total median reactivity increased again in 2001 as concentrations of most of the measured compounds, especially propylene and ethylene, increased.

482011041 San Jacinto Monument (Figs. I-103 through I-106, App. I)

Propylene is by far the biggest contributor to high reactivity at the San Jacinto Monument

monitor, and accounts for over 80 percent of the total for high reactivity days. Elevated propylene concentrations appear on the wind direction plot for winds coming from the southwest, between 160° and 270°. Many of the closest propylene sources are located within this wind degree range, although there are several sources located outside this range. Data has only been collected at this site for the years 2000 to 2001, and a significant increase in propylene emissions in 2001 led to a much greater median reactivity in 2001 than in 2000.

The wind direction analysis for most of the monitors located in the HGA area showed that emissions from the Ship Channel area affected the measured concentrations of several chemicals, most notably ethylene and propylene. Many of the monitors show the highest concentrations of these chemicals in wind blowing from the direction of the Ship Channel.

Summary and Conclusions

This analysis of the canister data collected in HGA and BPA produced results that are similar to the results from the Auto-GC analysis. The twelve compounds that are generally responsible for high reactivity based on the Auto-GC results are also responsible for high reactivity according to the canister data, in particular propylene and ethylene. The wind direction analysis performed for each of the monitors that collected canister data identified groups of sources that may have been responsible for emitting the compound that contributed most to high reactivity at that monitor, but there were several monitors where the wind directions identified by the analysis did not encompass all of the nearby sources. For eight of the 24 TCEQ monitors that were used in this analysis, the total median reactivity was lowest in the last year of data collection that occurred at each monitor between 1997 and 2001, indicating an overall decrease in concentrations of certain compounds. For the remaining 16 TCEQ monitors, the lowest median reactivity was observed in a year other than the last year, which means that concentrations of some compounds did not decrease overall. The yearly data for all of the SETRPC monitors showed that concentrations declined to their lowest value in the last year of collected data used for this analysis.

For many of the monitors, either ethylene or propylene accounted for the highest percentage of total reactivity for high reactivity days. For monitors located in the HGA area, wind direction analysis has indicated that the emissions from the Ship Channel area have contributed to high ethylene and propylene concentrations.

References

Carter, William P. L. (October 25, 2002). MIR Reactivity Spreadsheet. Available via ftp: <ftp://ftp.cert.ucr.edu/pub/carter/SAPRC99/r02tab1.xls> (Accessed January 2003).